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Quantum Mechanical Calculations of the Second Virial Coefficients for Hydrogen

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CONTENTS

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Quantum mechanical second virial coefficients of dilute ortho and para hydrogen have been calculated for the case of a Lennard-Jones potential. These computations cover the temperature range from 0 °K to 80 °K. Special attention is paid to the behaviour of the Boltzmann and exchange contributions. The purely statistical contribution to the ortho-para difference is shown to vanish to three decimal places by about 10.5 °K. Comparison with experimental data indicates that considerable improvement in the potential function and inclusion of non-spherical terms will be required at the low temperatures considered here.

Key Words - Second Virial Coefficient, Quantum Mechanics, Hydrogen, Equation of State, Statistical Mechanics, Intermolecular Potential

1. INTRODUCTION

This note summarizes the initial calculations in a program aimed at accurate computation of the quantum mechanical second virial coefficient of dilute hydrogen. Ultimately, it is planned to carry out the computations over the complete range of temperatures from absolute zero up to the classical region. The work reported here extends up to 80 °K. Both the ortho and para forms are considered as well as their mixtures. While present calculations are concerned with spherical potential fields for hydrogen, it is hoped to extend them eventually to include the effects of non-spherical potential terms.

One of the aims of this work is to provide a sound theoretical basis for the evaluation and correlation of existing data on hydrogen now being carried out by the Cryogenic Data Center at the National Bureau of Standards Boulder laboratory. Our studies would also aid in supplying information in ranges where the data are limited in accuracy or non-existent.

These calculations can be considered as part of a larger program aimed at searching for an optimum intermolecular potential function suitable for determining not only the second virial coefficient but also the transport properties of hydrogen. In such an undertaking accurate calculations for the Lennard-Jones potential seem the logical starting point due to its widespread use.

2. BACKGROUND

The best previous quantum mechanical calculation of the second virial coefficient for H_2 is to be found in the work of Cohen, Offerhaus, van Leeuwen, Roos, and de Boer [1] (which also contains calculations of the various transport properties), hereafter referred to as COLRB. Their work is based on a spherically symmetric potential field assumed the same for all states of the molecule so that the para-para, ortho-ortho and para-ortho interactions are all represented by the same molecular field. The second virial coefficient is then expressed in terms of integrals which involve phase-shifts arising from the characterization of the asymptotic behaviour of the wave function of relative motion of two H_2 molecules. They chose as the potential field the well-known Lennard-Jones form

$$\mathcal{P}(r) = 4\epsilon \left\{ (\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6} \right\}$$

where ϵ is the depth of the potential well, and σ is the "size" of the molecule (the radius at which the potential is zero).

The values used for these parameters were obtained previously from high temperature data by de Boer [2] who found

$$\epsilon/K = 37.00 \text{ }^{\circ}K$$
$$N \sigma^{3} = 15.12 \text{ cm}^{3}/mol$$

from which he obtained, using the 1952 values of Dumond and Cohen for Avogadro's number N, and the Boltzmann constant K, the values

$$\epsilon = 31.88 \times 10^{-4} ev$$
$$\sigma = 2.928 \text{ Å}$$

The Schroedinger equation for the relative motion of two particles in this potential field must then be integrated numerically for each value of energy (wave number k) and angular momentum ℓ) out to a sufficiently

large value of the radius to determine the asymptotic behaviour and thus the phase shifts (η (k)). The presence of bound states, if any, and their values must be ascertained. In their calculations COLRB used values for the phase shifts obtained by Van Wijngaarden and Duijvestijn using an electronic computer and calculating to three decimal places. They obtained these phase shifts for values of k*, the reduced wave number ($k^* = \sigma \frac{\sqrt{mE}}{\hbar} = k\sigma$), from 0 to 4.0 at intervals of 0.1, and from 4.0 to 8.0 at intervals of 0.2 and for values of the angular momentum quantum number, ℓ, from 0 to 23.

The potential field they chose was found to contain two discrete energy levels and these were determined to be as follows:

$$\ell = 0 \quad ; \quad -3.147 \times 10^{-4} \text{ eV} = -3.651°K$$
$$\ell = 1 \quad ; \quad -1.227 \times 10^{-4} \text{ eV} = -1.424°K$$

For these two values of the angular momentum the phase shifts go to the value π instead of zero as k* goes to zero.

The second virial coefficients, $B^* = B/N\sigma^3$ were computed for para-hydrogen (pH_2) and ortho-hydrogen (oH_2) in terms of virials for Bose and Fermi statistics, using the following relations derived by consideration of the degeneracies occuring in the two forms:

(1a)
$$B^*_{pH_2} = B^*_s$$

(1b)
$$B^*_{oH_2} = \frac{5}{9} B^*_s + \frac{4}{9} B^*_a$$

where

$$B^*_{\substack{s \\ a}} = \mp |B^*_{id}| - \frac{2\Lambda^{*3}}{\pi^{5/2} T^{*3/2}} \int_0^\infty e^{-\gamma^2} \left\{ \sum_{\substack{\ell = \text{even nos.} \\ \ell = \text{odd nos.}}} (2\ell+1)\eta_\ell (k) \right\} \gamma \, d\gamma$$

$$- \frac{\Lambda^{*3}}{\pi^{3/2} T^{*3/2}} \sum_{\substack{\ell = \text{even nos.} \\ \ell = \text{odd nos.}}} (2\ell + 1) (e^{-E_\ell^*/T^*} - 1)$$

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in which the subscripts s or a and the sums over ι-even or ι-odd refer to Bose-Einstein (symmetric) or Fermi-Dirac (antisymmetric) statistics, respectively. The various reduced quantities involved are:

$$\Lambda^* = h/\sigma\sqrt{m\epsilon}$$

$$T^* = T \ (K/\epsilon)$$

$$E_\iota^* = E_\iota/\epsilon$$

$$\gamma^2 = \hbar^2 k^2 /mKT$$

The first term, B^*_{id}, is the second virial coefficient of an ideal quantum gas and has the magnitude $\Lambda^{*3} / 16\pi^{3/2} T^{*3/2}$. The second term is the contribution of the continuum states of molecules interacting through a potential, while the last term gives the contribution of the bound states of energies E_ι.

For mixtures of para and ortho hydrogen these authors use the expression

$$B^*_{mix} = \chi_p^2 \ B^*_{pH_2} + 2\chi_p\chi_o \ B^*_{p-oH_2} + \chi_o^2 \ B^*_{oH_2}$$

where $B^*_{p-oH_2} = 1/2 \ (B^*_s + B^*_a)$ and the χ's are the percentages of each species in the mixture.

Results are given at temperatures of 1.85°K and at intervals of 3.7° from 3.7°K to 37°K. (See table I) Comparison with experiments indicated that their results were about 10% too large at low temperatures. COLRB believed the discrepancy to be due largely to the lack of knowledge of the extent of influence of non-spherical terms in the potential over the temperature range involved. To investigate this possibility further these authors applied the Wang Chang [3] classical non-spherical corrections to the high temperature theoretical curve. They then redetermined the Lennard-Jones parameters from the resulting curve. The low temperature discrepancy between theory and experiment was then reduced to 3%. However, they now considered the parameters to be of doubtful meaning and the procedure was regarded as unsatisfactory since the non-spherical corrections should also be applied at low T.

3. CALCULATIONS

Our initial calculations for the quantum mechanical second virial coefficients are, in general, an amplification of the computations of COLRB. with several alterations and improvements. We employ a

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formulation in terms of the phase shifts, as they have done, but have used a different arrangement of Eq. (1) in which we have separated the contribution of a Boltzmann gas (B-direct) from the effects due to quantum statistics (B-exchange). [5]

For a gas of spin S we may then write the virial as a sum of two terms:

$$(2) \qquad B = B_{direct} + B_{exch}$$

where:

$$(3) \quad B_{direct} = -2^{1/2} N \lambda_T^3 \sum_\ell (2\ell+1) \left\{ \frac{\lambda_T^2}{\pi^2} \int_0^\infty dk \; k \; \eta_\ell(k) \, e^{-\frac{\lambda_T^2}{2\pi} k^2} \right.$$
$$\left. + \sum_n [e^{-\beta E_{n,\ell}} - 1] \right\}$$

and

$$(4) \quad B_{exch} = \mp \frac{2^{1/2} N \lambda_T^3}{(2S+1)} \sum_\ell (-1)^\ell (2\ell+1) \left\{ \frac{\lambda_T^2}{\pi^2} \int_0^\infty dk \; k \; \eta_\ell(k) e^{-\frac{\lambda_T^2}{2\pi} k^2} \right.$$
$$\left. + \sum_n [e^{-\beta E_{n,\ell}} - 1] \right\} \mp \frac{N \lambda_T^3}{2^{5/2}(2S+1)}$$

Here $\lambda_T = h / \sqrt{2\pi mKT}$, $\beta = 1/KT$, and $E_{n,\ell}$ is the energy of the nth bound state for angular momentum ℓ. In B_{exch} the upper signs refer to the symmetrical (Bose) statistics while the lower signs refer to the Fermi or antisymmetric case.

Analysis of the behaviour of the B_{exch} term [4] as well as numerical evaluations for various cases [5, 6] demonstrates that the quantum statistical effects embodied in it are sharply suppressed with rising temperature whenever a strong repulsive core is present in the potential. In fact, above a few degrees Kelvin the Lennard-Jones gas may be regarded as effectively a Boltzmann gas.

This equation also has the advantage of displaying the very simple dependence of the second virial coefficient on the spin. In addition, the subtraction involved between the interacting gas and the ideal quantum gas contributions in evaluating the B_{exch} term makes

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the effect of numerical inaccuracies quite conspicuous. That is, they cause the subtraction to be inexact as $B_{exch} \to 0$ and erratic results occur of the order of magnitude of the digit in error.

Turning our attention now to hydrogen we first consider the case of the para modification. The spins of the two hydrogen atoms in the molecule are opposed giving a net spin of zero and in its ground state the rotational quantum number J is zero. We thus have no degeneracy and only symmetric wave functions are allowed. That is, we have a spinless Bose gas and

$$(5) \quad B_{pH_2} = B_{direct} + B_{exch}^{Bose} \ (S=0)$$

where B_{exch}^{Bose} is calculated setting S = 0 and using the upper signs in Eq. (4).

For ortho hydrogen the situation is more complicated. Since the spins of the atoms are parallel they must be added, giving a spin of 1 for the H_2 molecule. Thus, we have a 3-fold degenerate state, where the z component of spin, of interest in a collision of two molecules, can be 1, 0, or -1. In addition, the ground state of the ortho molecule has rotational quantum number J = 1, also three fold degenerate. The result is thus 9 possible states for the molecule and $9^2 = 81$ possibilities when two molecules interact. Considering M = J + S for each molecule we have the possible M values of 2 (which is 5-fold degenerate), 1 (3-fold degenerate), or 0. Collisions between molecules of different M values will give only Boltzmann type terms, so no contributions will occur to b_{exch} in these cases. For two molecules of M = 2 (degeneracy 5) we get $5^2 = 25$ cases, between those of M = 1, $3^2 = 9$ cases, and between those of M = 0, 1 case. Thus for the exchange term, we get, averaging over all the possible cases:

$$B_{exch, \ oH_2} = B_{exch}^{Bose} \ (S=0) \left\{ \frac{1}{81} \left[25 \cdot \frac{1}{(2S+1)_{S=2}} + 9 \cdot \frac{1}{(2S+1)_{S=1}} + \frac{1}{(2S+1)_{S=0}} \right] \right\}$$

$$= \frac{B_{exch}^{Bose} \ (S=0)}{81} \left\{ \frac{25}{5} + \frac{9}{3} + \frac{1}{1} \right\}$$

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$$= \frac{1}{9} B^{Bose}_{exch} \quad (S=0)$$

and the total second virial coefficient for ortho hydrogen will be

$$(6) \quad B_{oH_2} = B_{direct} + \frac{1}{9} B^{Bose}_{exch} \quad (S=0)$$

Numerical improvements over the previous work of COLRB are as follows. First, the phase shifts are calculated to five figure accuracy in most cases instead of the three obtained by the previous workers. Second, instead of cutting off the sum over ℓ at an arbitrary value (23 in the previous work), we have included the phase shifts for all values of ℓ. This is done by finding for each k* the value of ℓ at which the phase shift computed by integration of the Schroedinger equation agrees with the value obtained by the Born approximation to within one digit in the 4th decimal place. The sum over the Born approximation values of the phase shifts from this value of ℓ to $\ell = \infty$ can then be evaluated analytically.

The third numerical improvement was to increase the range of k* values and to decrease the interval size between k* values used in the numerical integration of Eqs. (3) and (4). We have calculated phase shifts up to k* = 16, twice the range of COLRB at intervals of 1/16, interpolating the sums over them to 1/64. This has the effect of improving the accuracy of the virial coefficients obtained at the low temperatures and of allowing their calculation at higher temperatures than previously obtained. We give values to 80°K.

The values of the energies of the bound states in this molecule were obtained using a general computer program for calculating bound states for a Lennard-Jones potential of any given parameters which was written by J. E. Kilpatrick, M. Fraser and S. Y. Larsen(unpublished). Using the de Boer parameters these energies were calculated to seven digits, as contrasted to the four digits used by COLRB. This is necessary in order to obtain more digits in the low temperature values of the virial as can be easily seen by examining the individual terms given in Table II. The lower bound state was determined to be at −3.651296°K, agreeing with the COLRB value to the four digits they used. The upper one we have computed is at −1.422061°K, which differs from the COLRB value in the fourth digit. The behaviour of the exchange term is especially sensitive to these values and displays conspicuously

the effect of an error. In this case, the erroneous digit caused B_{exch} to change sign when it became of the order of magnitude of the decimal digit affected by the error.

Examination of the results obtained indicates general agreement with the results of COLRB, as one would expect. Table I gives our results for para and ortho H_2 compared to COLRB's calculations. At the lowest temperature shown, 1.85°K, our result for para H_2 is about 10 cm^3/mole lower (only about 0.1%) than the earlier calculations, while at the upper end of their range, 37°K, the change is about 1.6 cm^3/mole or about 3% change in the direction of the experimental values, which are some 7% to 8% lower still. It is interesting to note that 7% is about the amount of improvement that was made in the calculations of COLRB by employing the classical non-spherical correction at high T. Thus, if applied to our curve, agreement with experiment within about a per cent or so would result, but this must be regarded as rather fortuitous at the present stage of computation. Table III gives our results for B_{direct}, B_{exch}^{Bose}, and the ortho-para difference up to 80°K. The part of the ortho-para difference which is due to statistics alone (that is, the potential function is assumed the same for both) depends only on B_{exch} which can be seen to have vanished to the accuracy we have calculated by about 10.5°K. We emphasize, however, that if the potential function does differ for the different rotational states, as is the case in reality, the ortho-para difference would persist to higher temperatures.

It should be noted here that at least two re-determinations of the Lennard-Jones parameters for H_2 have been made since the calculations of COLRB. Michels, De Graaff and Ten Seldam[7] made a new fitting of these parameters based on experimental data obtained in their laboratory[8] for the temperature range −175°C to +150°C. It was not possible to find a set of values for the parameters which would enable the fitting of the virials within the experimental accuracy over the whole temperature range involved, even with the introduction of high temperature corrections for the non-spherical effects. However, the best set of values was given as

$$\epsilon/K = 36.7°K$$
$$N\sigma^3 = 15.60 \text{ cm}^3/\text{mol}$$

It should be noted that the expression for the second virial coefficient at high T used by these authors is incorrect, containing a term for the ideal gas (statistical) contribution which can be shown to have been cancelled out by the two-body exchange effects at this temperature[4].

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It is not likely that this would account for the whole difficulty in obtaining a fit over the range of temperatures involved, but the parameter values given by these authors must be considered somewhat unsatisfactory.

More recently, Diller and Mason [9] fitted viscosity data and obtained the values

$$\epsilon/K = 37.2°k$$

$$\sigma = 2.97 \text{ Å}$$

using mainly the date of Coremans, et. al., [10] and Johnston and McCloskey [11] but also measurements of van Itterbeek, et. al., [12] and Becker and Misenta [13]. It has been known for some time, for example in the case of He, that the best parameters or even forms of potentials for fitting the second virial are not the best for the viscosity, [14] so it is not surprising that the values of Diller and Mason are different from those of Michels, et. al. The main conclusion about them which can be drawn at present is that the question of optimum potential parameters for H_2 is still an open one. In fact, more recently H. Hanley and M. Klein of NBS (unpublished work) have examined the possibility of fitting the data over a large temperature range in the classical region by means of various three-parameter potentials and concluded that it was not possible to do so with any of them.

In order to extend our calculations over the complete range of temperatures we have recently computed new phase shifts extending out to a value of $k\sigma = 42.5$. These should allow the computation of the second virial coefficient up to the classical region.

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Table 1a

Second Virial Coefficients of Para and Ortho Hydrogen

T*	T°K	B_{pH_2} (cm³ / mole)		B_{oH_2} (cm³ / mole)	
		COLRB Calculation[a]	This Calculation	COLRB Calculation[a]	This Calculation
.05	1.85	-9986.	-9996.5	-8887.	-8888.2
.10	3.7	-1786.	-1792.75	-1771.	-1776.62
.15	5.55		- 869.956		- 869.183
.20	7.4	- 547.4	- 552.893	- 547.6	- 552.835
.25	9.25		- 397.120		- 397.115
.30	11.1	- 301.9	- 305.71	- 301.9	- 305.71
.35	12.95		- 246.00		- 246.00

a) Data from Reference 1.

Table 1b

Second Virial Coefficients of Hydrogen – Boltzmann Region

		B (cm^3/mole)		
T*	T°K	COLRB Calculation[c]	This Calculation	Experimental
.40	14.8	-201.1	-204.11	-237 [a]
.45	16.65		-173.17	-191 [a]
.50	18.5	-146.8	-149.42	-174 [a]
.55	20.35		-130.65	-152 [a]
.60	22.2	-113.2	-115.44	-127.8[b]
.65	24.05		-102.886	-112.5
.70	25.9	- 90.3	- 92.348	-100.9
.75	27.75		- 83.383	- 90.90
.80	29.6	- 73.8	- 75.666	- 82.41
.85	31.45		- 68.956	- 75.03
.90	33.3	- 61.4	- 63.070	- 68.52
.95	35.15		- 57.866	- 62.72
1.00	37.0	- 51.6	- 53.233	- 57.54
1.081	40.0		- 46.716	- 50.32
1.216	45.0		- 37.950	- 40.80
1.351	50.0		- 31.08	- 33.39
1.486	55.0		- 25.56	- 27.48
1.622	60.0		- 21.02	- 22.70
1.757	65.0		- 17.2	- 18.64
1.892	70.0		- 14.0	- 15.22
2.027	75.0		- 11.	- 12.42
2.162	80.0		- 9.	- 9.88

a) Values interpolated from data in Reference 15.

b) Data from this temperature up from Reference 16.

c) Data from Reference 1.

Table II

Contributions to the Second Virial Coefficient of H_2

T°(K)	B_{id}(Bose)	Bound States		Continuum States	
		$\ell = 0$	$\ell = 1$	Direct	Exchange (Bose)
1.85	-78.695405	-7802.890	-4370.128	-2663.10	548.20
3.70	-27.823027	-749.1004	-625.8790	-1087.119	71.296
5.55	-15.144937	-225.5303	-212.3051	-650.169	20.887
7.40	-9.8369259	-100.4005	-100.0425	-452.606	9.950
9.25	-7.0387311	-54.50686	-56.14656	-341.788	6.213
11.10	-5.3545441	-33.36971	-35.12978	-271.457	4.474
12.95	-4.2491526	-22.14433	-23.67312	-223.092	3.485
14.80	-3.4778785	-15.57015	-16.83619	-187.905	2.845
16.65	-2.9146448	-11.43479	-12.47410	-161.215	2.395
18.50	-2.4485673	-8.687746	-9.544116	-140.308	2.060
20.35	-2.1570507	-6.782768	-7.494074	-123.509	1.801
22.20	-1.8931173	-5.414967	-6.011294	-109.729	1.595
24.05	-1.6789369	-4.404239	-4.908872	-98.229	1.427
25.90	-1.5023023	-3.639124	-4.069998	-88.494	1.287
27.75	-1.3546044	-3.047906	-3.418883	-80.150	1.169
29.60	-1.2296157	-2.582891	-2.904766	-72.922	1.069
31.45	-1.1227317	-2.211448	-2.492702	-66.604	.982
33.30	-1.0304825	-1.910693	-2.158052	-61.035	.907
35.15	-.95020871	-1.664227	-1.883076	-56.092	.841
37.00	-.87984145	-1.460074	-1.654758	-51.676	.782

Table III

Direct and Exchange Second Virial Coefficients for H_2

$T(^\circ K)$	B_{direct} (cm^3/mole)	B^{Bose}_{exch}	$(B_{oH_2} - B_{pH_2})$
1.85	−8749.6	−1246.9	+1108.3
3.70	−1774.61	− 18.14	+ 16.13
5.55	− 869.086	− .870	+ 0.773
7.4	− 552.828	− .065	+ 0.058
9.25	− 397.114	− .006	+ 0.005
11.1	− 305.707	− .000	0.000

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